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CHEMICAL OXIDATION OF ORGANIC CONTAMINANTS IN WATER SUPPLIES

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INTRODUCTION

The presence of trace organic pollutants in natural water supplies has become of increasing significance in the past several years. These organic materials may result in many problems in the waterworks industry. They can cause taste and odor problems, off tastes in fish flesh, fouling of ion exchange resins, and foaming (1). In addition, they may interfere with coagulation, create high chlorine and activated carbon demands, adversely affect aquatic forms that support higher aquatic life, and are at times toxic to fish and possibly to man (2).

Although usually present in very small amounts, the total organic material recovered from water sources has been as high as three mg/l (3). The sources of these organic compounds include sewage, industrial wastes, decaying vegetation, surface runoff, agricultural fertilizers, pesticides, detergents, microorganisms and their products of metabolism, chemicals applied to bodies of water to kill fish and aquatic plants, and chemicals added to prevent evaporation losses (4).

Investigations have shown that conventional water treatment processes have but limited success in removing organic

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materials of this nature from water (5). A new term used for them is organic refractories.

Chemical oxidation methods have long been employed for the control of tastes and odors due to trace organic contaminants in water supplies. Aeration to supply oxygen was one of the first methods utilized and is still used today. Chlorine or its derivatives are added in most water treatment plants in the United States as disinfectants, but they are also used to relieve taste and odor problems. Grigoropoulos (6) reported that organic extracts from a river used for public water supplies were resistant to chemical oxidation with chlorine and chlorine dioxide.

Ozone, one of the most powerful oxidants, has been used for several years both for taste and odor control and as a disinfectant. It has also been shown to be helpful in reducing the foaming caused by trace organics (7).

Potassium permanganate is reported to be useful as a strong oxidant for water treatment. In 1960 new application techniques for potassium permanganate were developed. Manufacturing improvements by a large chemical company made potassium permanganate an economical chemical for use in water treatment plants. Since that time it has been applied in thirty-eight states and fourteen foreign countries (8). It has been used for two primary functions of taste and odor control and iron and manganese removal. At least three other benefits are reported to be derived from its use. The manganese dioxide

hydrate acts as a coagulant aid, and potassium permanganate acts as both a biocide and an algicide (9).

Cherry (10) reported the use of permanganate in conjunction with activated carbon in Cedar Rapids, Iowa, to reduce tastes and odors to a level which could not be attained by carbon alone. A carbon dose of 83 ppm reduced the threshold odor from 60 to 14. An average 10 ppm concentration of permanganate, however, in conjunction with 50 ppm of carbon, reduced threshold odors from an initial range of 400 to 2000 to values of 3 to 5 during times of high odor problems.

Smith (11) reported similar experiences at Waxahachie, Texas. Carbon alone did not reduce the odors, but permanganate doses of 0.75 mg/l together with 5 mg/l carbon reduced the threshold odors to less than 2. The cost of the permanganate-carbon treatment was only 10 percent of the cost of the previous unsuccessful carbon treatment.

Little information is available on the actual reactions involved in the utilization of potassium permanganate in water treatment processes. The chemical literature contains many conflicting theories and mechanisms for permanganate oxidation of specific organic materials, and no studies have been made on permanganate oxidation of complex mixtures of refractory materials taken from water supplies.

The purpose of this research was to investigate the chemical oxidation of organic refractories with potassium permanganate. Soluble trace organic contaminants used in the study were extracted from a surface water supply using a

modified carbon filter technique to collect sizable quantities of the organic refractories. The organic materials thus separated from their natural environment were brought into the laboratory, characterized, and studied under controlled conditions. Permanganate oxidation of various organic refractories was investigated in deionized water and in modified natural river water systems. Controlled amounts and types of organics were reacted with permanganate under controlled conditions of pH, temperature, time and concentrations. Carbon chloroform extracts (CCE) and carbon alcohol extracts (CAE) were the two major groupings of organic refractories investigated.

RIVER ORGANICS RECOVERY AND CHARACTERIZATION

The organic refractory material utilized in this study was extracted from the Missouri River at the intake of the St. Louis County Water Company Central Plant in St. Louis County, Missouri. A modification of the carbon filter technique, similar to that employed by Myrick (12) and Dornbush (13), was used. The technique involved preclarification followed by adsorption of the organics with two carbon filters in series. Pretreatment was necessary due to the high turbidity of the Missouri River water and because adsorption on activated carbon has been reported to be more effective when turbidity is low (14). Pretreatment consisted of sedimentation and diatomaceous earth filtration.

Pretreated water was pumped through the first carbon filter in the two filter series at the normal pH of the river

water. The pH of the effluent from the first carbon filter was then reduced to 3.2 with sulfuric acid. The acidified water was made to flow through the second carbon filter, and the effluent was wasted to the river. Mega filters holding 1.3 cubic feet of carbon were used in order to obtain a sufficiently large sample of organic material. A diagramatic sketch of the system is shown in Figure 1.

Two small standard size carbon filters (15) were operated in parallel with the two large carbon filters. The purpose of these monitoring filters was to provide a comparison of results of the modified technique with those of the standard technique. The standard filters were preceded by sand filters for pre-treatment to remove turbidity.

Upon completion of carbon filtration of 103,000 gallons of river water, the carbon was removed from the filters and dried in the laboratory at room temperature. It was then placed in modified Soxhlet extractors, where the organic material was desorbed with solvents. The two solvents used for serial extraction were chloroform and ethanol. A carbon blank was analyzed in a similar manner to determine the amounts of extractable organics on the original carbon. This provided a correction factor which was applied to all recovery calculations.

Four organic fractions were obtained from the two mega carbon filters, as follows:

(a) Chloroform extract from the first (pH 7.7) carbon filter, or CCE-B.

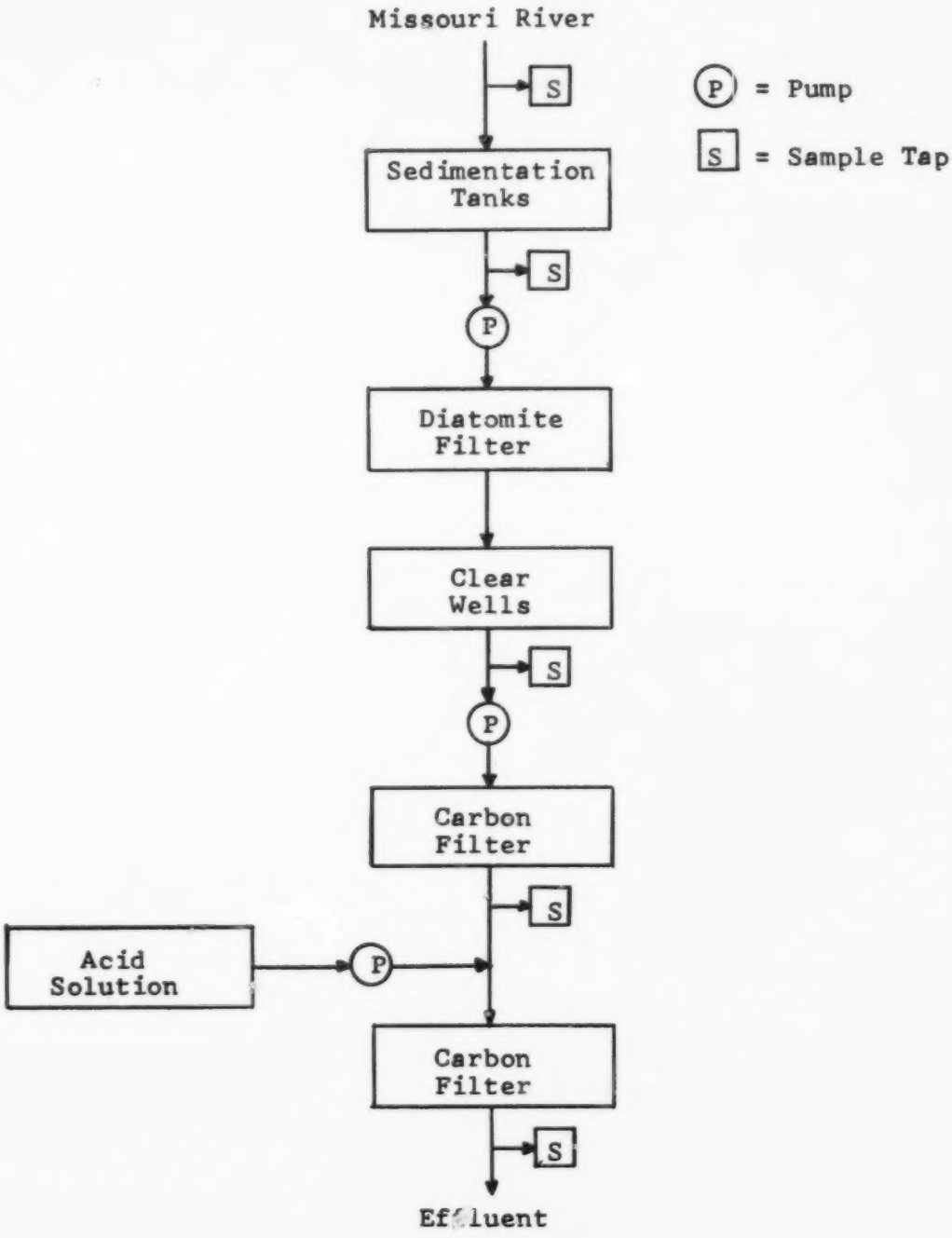

FIGURE 1

SCHEMATIC DIAGRAM OF MODIFIED CARBON FILTER SETUP FOR COLLECTION OF ORGANIC REFRACTORIES

(b) Ethanol extract from the first carbon filter, or CAE-B.

(c) Chloroform extract from the second (pH 3.2) carbon filter, or CCE-A.

(d) Ethanol extract from the second filter, or CAE-A.

The postscripts A and B used above refer to the acidic or basic character of the water from which the organic matter was recovered.

The concentrations of organic refractory materials recovered by the two carbon filters in series and by the monitoring filters are shown in Table 1. It is noted that the first carbon filter recovered organics in about the same range of concentrations as did the monitoring filters. It is significant that the second carbon filter, with the pH of the water lowered to about 3.2 prior to extraction, recovered greater amounts of organic materials than did the first carbon filter. The second filter recovered 444 ppb or nearly two-thirds of the total organic refractories recovered. The CCE-B, which is the fraction most commonly referred to and that fraction for which a recommended limit has been set (15), was only 71 ppb or about 10 percent of the total organic refractories recovered by the modified carbon filter technique.

The organic refractories collected from the Missouri River were placed into solution in the laboratory by the use of a high speed mixer. Two types of water used in preparing stock solutions were distilled-deionized water and modified natural river water. Initial permanganate oxidation studies were carried out in solutions of organics dissolved in

TABLE 1

QUANTITIES OF ORGANIC REFRACTORIES RECOVERED*

Refractory Fractions	Weight Recovered in grams	Concentration Recovered in ppb
First Monitoring Filter		
CCE	0.98	66
CAE	3.46	233
Total	4.44	299
Second Monitoring Filter		
CCE	0.67	45
CAE	2.79	187
Total	3.46	232
First Carbon Filter		
CCE-B	27.9	71
CAE-B	65.1	166
Subtotal	93.0	237
Second Carbon Filter		
CCE-A	23.	59
CAE-A	151.	385
Subtotal	174.	444
Totals for both Filters		
CCE-B + CCE-A	51.	130
CAE-B + CAE-A	216.	551
Total	267.	681

*Corrected for amount of organics recovered from carbon blank. One-half of the amount of organics found on the blank, on a carbon dry weight basis, was subtracted from the amount of organics recovered from the filters.

Blank: CCE = .0075 gm
CAE = .2556 gm

distilled-deionized water. In order to investigate the effect of soluble inorganic constituents in natural river water on the reactions of potassium permanganate, a modified natural river water was prepared. The preparation consisted of removing the turbidity and organic matter from Missouri River water.

In addition to stock solutions of the four organic fractions, CCE-B, CCE-A, CAE-B and CAE-A, a composite solution was prepared consisting of the percent concentrations of the four fractions found in the original sampling.

The following characteristics of the organics are shown in Table 2: pH, COD, threshold odor numbers, color values, carbon content, and fish toxicity results. The COD values are shown as mg COD per mg organic refractory. The values ranged from 1.29 mg/mg for the CAE-A fraction to 1.87 mg/mg for the CCE-B fraction. The pH of the solutions varied from 4.1 to 5.1, which indicated the acidic nature of many of the contaminants. The threshold odor values ranged from 70 to 198 ppb at 24°C. and from 30 to 118 ppb at 60°C. It is significant to note that the alcohol fractions, and the acid alcohol fraction in particular, were more odorous than the chloroform fractions. Colors of solutions of the organics were determined by the tristimulus method (16) using a Bausch and Lomb 505 spectrophotometer. Ten selected ordinates were used to determine the tristimulus values. The color determinations were made on 1000 mg/l solutions of the organics in chloroform or ethanol, depending on the type of refractory. The results are presented as the four color characteristics: dominant wavelength, hue,

TABLE 2

CHARACTERISTICS OF SOLUTIONS OF ORGANIC REFRACTORIES

	CCE-B	CCE-A	CAE-B	CAE-A	Composite
COD - mg/mg	1.87	1.66	1.36	1.29	1.38 (1.40)*
pH	5.1	4.6	4.8	4.1	4.3
Threshold odor					
24°C. - ppb	198	198	166	70	128 (142)*
60°C. - ppb	100	118	70	38	59 (75)*
Color**					
Dominant wavelength - mμ	582	573	576	578	-
Hue	Yellowish-Orange	Greenish-Yellow	Yellow	Yellow	
Percent luminance	92.7	82.5	65.8	57.0	-
Percent purity	11	30	40	49	-
Carbon content mg/mg organic	0.474	0.448	0.328	0.356	-
Fish Toxicity-- mg/l					
24-hr. TL_m	17.1	93	(90-900)***	(90-900)***	
96-hr. TL_m	11.7	90	(90-900)***	(90-900)***	

*Calculated values in parentheses.
**Color determined on 1000 mg/l solutions of organics in chloroform and ethanol, respectively.
***A range is indicated based upon a screening test.

luminance and purity. The dominant wavelengths and hues for the four fractions were relatively similar, ranging from 573 to 582 mμ (greenish yellow to yellowish orange).

Carbon determinations were made using the Van Slyke method (17) and the results are reported as mg carbon per mg organic refractory. The CCE contained greater percentages of carbon than did the CAE.

Results of the toxicity studies on bluegills are reported in 24-hour TL_m and 96-hour TL_m values. The CCE-B fraction was much more toxic to fish than the CCE-A or the CAE fractions.

The results of ether solubility separation determinations to further characterize the organics are shown in Table 3. These results are mean values of several determinations. In the CCE-B fraction the neutral and water soluble groups were predominant whereas in the CCE-A fractions, the water solubles and the strong acids predominated. The CCE-B fraction contained more neutrals and more weak acids than the CCE-A fraction, but less strong acids, water solubles, and ether insolubles. The amines and amphoterics in both fractions were similar in quantity, the amines being very small. In both neutral fractions the oxygenated materials were predominant. The alcohol fractions were predominantly ether insoluble.

PERMANGANATE OXIDATION PROCEDURES

Reactions of organic refractories with potassium permanganate were studied using residual permanganate and organoleptic determinations. The effects of seven variables on the

TABLE 3

CHEMICAL GROUP SEPARATION

Percent of Total Extract

	CCE-B	CCE-A	CAE-B	CAE-A
Ether Insolubles (EI)	10.0	14.1	76.2	65.0
Water Solubles (WS)	21.4	31.0	4.7	9.5
Amines (Am)	1.3	0.1	1.0	1.8
Amphoterics (Amp)	10.0	12.6	1.7	1.8
Neutrals (N)	25.7	7.5	1.7	4.5
Strong Acids (SA)	12.8	23.0	4.7	8.5
Weak Acids (WA)	11.6	4.7	2.4	3.9
Total Recovery	92.8	93.0	92.4	95.0
Neutrals: (as % of neutrals)				
Aliphatic (Al)	3.1	19.6	-	-
Aromatic (Ar)	2.6	3.4	-	-
Oxygenated (Oxy)	92.2	50.2	-	-
Total Recovery	97.9	73.2	-	-

reaction were determined. These seven variables were:

(a) Concentration of the potassium permanganate,

(b) Type of organic refractory,

(c) Concentration of organic material,

(d) Time of reaction,

(e) pH,

(f) Temperature of the reaction, and

(g) Type of water used for the organic solution.

Potassium permanganate was employed in concentrations of 31.6, 47.4, 111 and 506 mg/l. These concentrations, which were used throughout the investigations, resulted from the addition of 2, 3, 7 and 32 ml of a 0.1 N stock solution of $KMnO_4$ respectively, to a 200 ml sample of water.

Laboratory solutions were made up of the recovered organic refractory materials. The five solutions thus used were the CCE-B, CCE-A, CAE-B and CAE-A fractions and the composite sample. Most of the studies were made at a concentration of 50 mg/l of organic material, but a series of studies at 10 mg/l was made to determine the effects of concentrations of organic refractories.

Variations of the reactions with time were studied by measuring the residual permanganate at specific time intervals after the reaction was initiated. The time intervals employed were 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours and 6 hours after the initiation of the reaction.

The two pH conditions used in the studies were a near neutral pH and a pH of 10. These two conditions were selected

because they represent the range of pH conditions normally found in water treatment plants. The near neutral pH was the pH of the samples unadjusted following organic material and permanganate additions. The pH was raised to 10 in higher pH studies by the addition of phosphate buffer solution.

The studies were carried out under controlled temperature conditions of 25°C. and 5°C. The reactions were carried out in 500 ml, ground glass stoppered, Erlenmeyer flasks. A total volume of 200 ml was used in each case. During the first 30 minutes the sample was stirred using magnetic stirrers. For the first five minutes a high speed of agitation was used to simulate rapid mix in a water treatment plant. For the next 25 minutes a slower stirring speed was used to simulate the slow mixing in a treatment plant.

PEAK HEIGHT ANALYSIS

At the desired time intervals ten milliliter samples were analyzed with a recording ultraviolet-visible spectrophotometer. The visible spectrum from 350 to 650 mμ was recorded, with the height of the permanganate peak at 526 mμ being used for the quantitative determination of residual permanganate.

In order to quantitatively measure residual permanganate in the presence of interferences from reaction products and reduced forms of manganese, it was necessary to use the peak height method of analysis developed by Wright (18). The principle of the method is illustrated in Figure 2. In A the concentration of compound X is proportional to the absorption A_x.

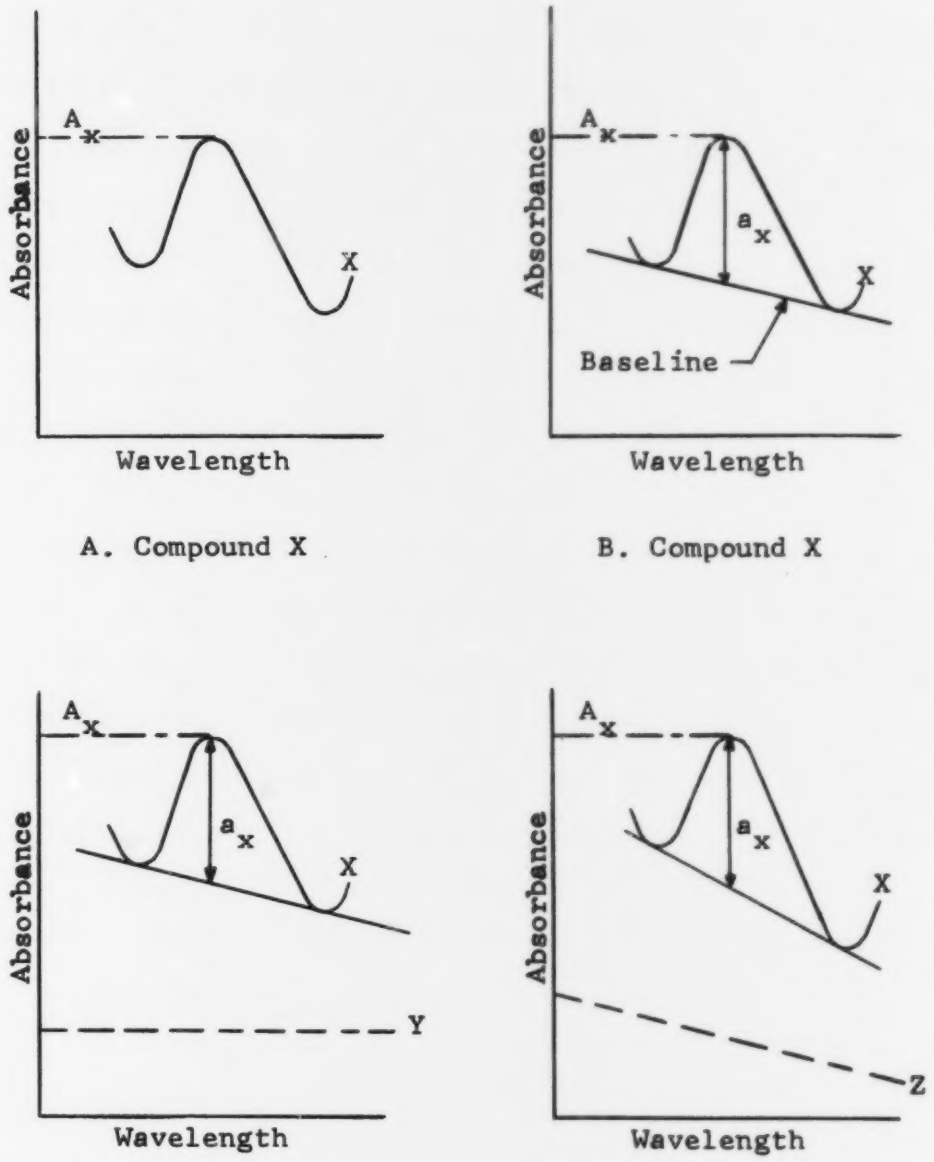

FIGURE 2

PRINCIPLE OF THE BASELINE ANALYSIS

In B a base line is drawn as shown and the concentration of X is also proportional to the absorption peak a_x.

In C a second compound Y, with a spectrum shown by the dotted line, increases the absolute absorption A_x of X but does not affect the value of the absorption peak a_x. Similarly in D the compound Z, with the spectrum shown as a dotted line, increases the value of A_x but has no effect on a_x. Thus, it is shown that if the absorption curves of the interfering substances are linear or nearly linear over the wavelength range of the absorption peak, the peak height absorbance, a_x, is proportional to the concentration.

A typical peak height analysis is shown in Figure 3.

A plot of permanganate concentration versus peak height was a straight line at concentrations between 0 and 60 mg/l $KMnO_4$ showing that Beer's Law was valid in this case. This plot is shown in Figure 4. The equation of the straight line:

$X = 318\ Y$ where: X = concentration of $KMnO_4$ in mg/l and
Y = peak height in absorbance units

was used to calculate residual permanganate concentrations from measured peak heights.

EXPERIMENTAL RESULTS

The experimental conditions for each of seven series of tests are shown in Table 4. Potassium permanganate was made to react with the four organic extracts and the composite sample under various conditions of pH, temperature, organic concentration, and permanganate concentration.

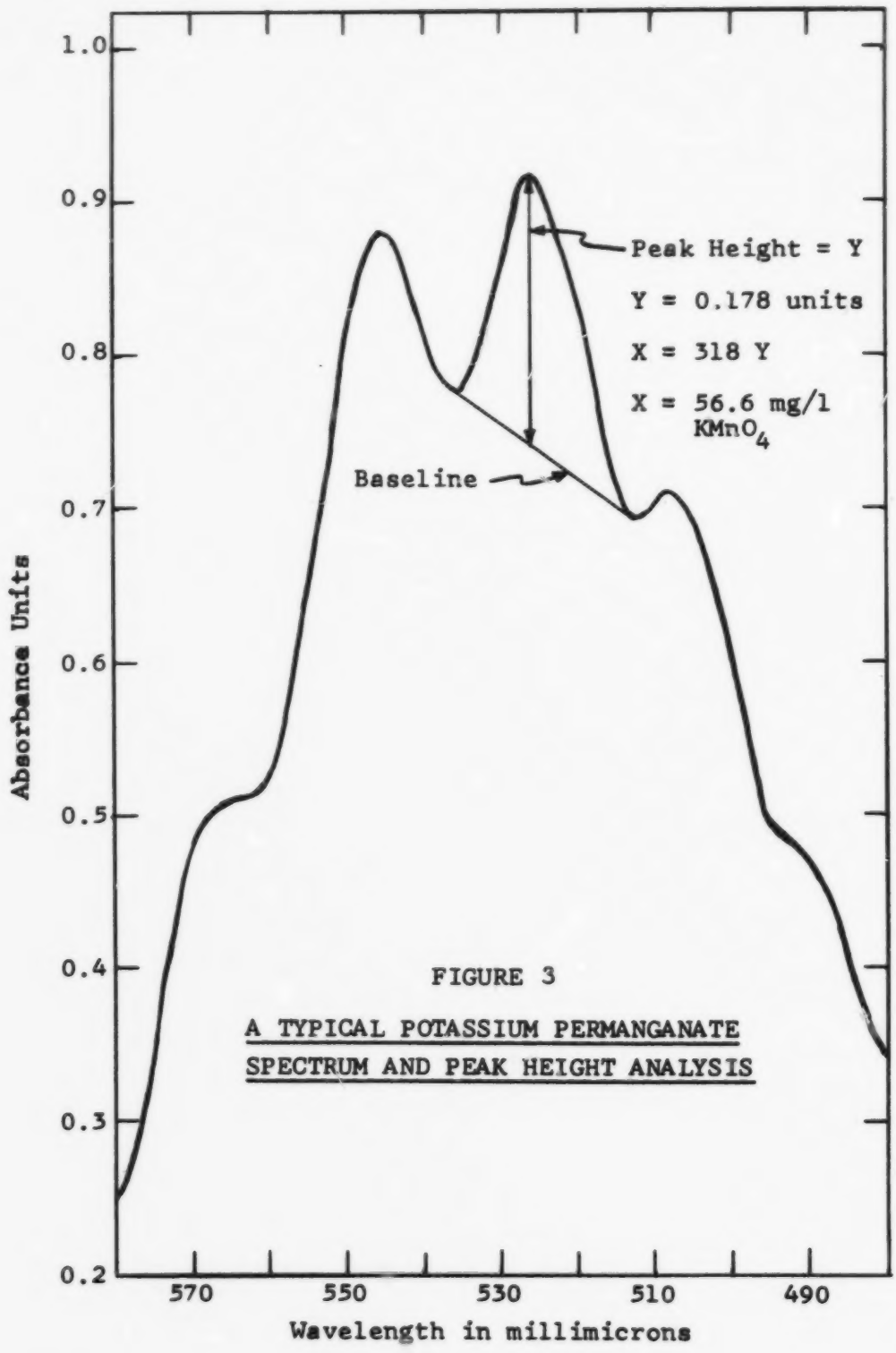

FIGURE 3

A TYPICAL POTASSIUM PERMANGANATE SPECTRUM AND PEAK HEIGHT ANALYSIS

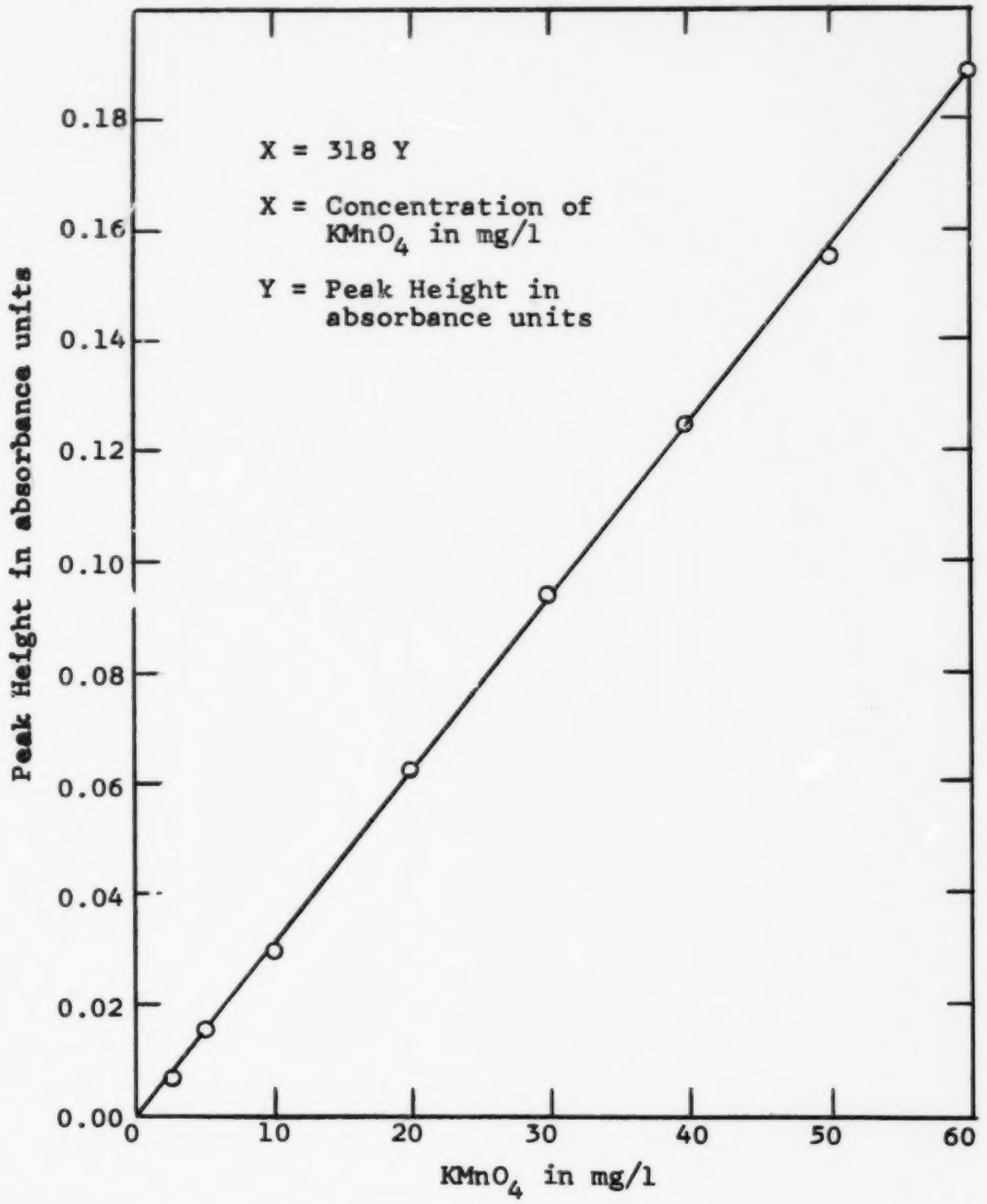

FIGURE 4

BEER'S LAW PLOT OF POTASSIUM PERMANGANATE ABSORBANCE PEAK HEIGHT ANALYSIS

TABLE 4

TEST CONDITIONS FOR OXIDATION REACTIONS

Series	Water to Which Organics Added	Temperature °C.	pH	Organic Concentration mg/l
1	Distilled-Deionized	25	4.0- 7.0	50
2	Distilled-Deionized	25	9.5-10.0	50
3	Distilled-Deionized	5	4.0- 7.0	50
4	Modified River	25	7.5- 8.5	50
5	Modified River	25	9.5-10.0	50
6	Modified River	5	7.5- 8.5	50
7	Modified River	25	7.5- 8.5	10

Figures 5, 6 and 7 show the general nature of the reactions with the five different types of organic refractories.

The CCE-B fraction was more readily oxidized than the other fractions in all cases. One possible explanation for this could be the greater amount of oxygenated neutral material in the CCE-B fraction. Table 3 shows 24.2 percent oxygenated neutral material in the CCE-B compared to less than 5 percent in all the other fractions. The oxygenated materials are reported (19) to be compounds such as aldehydes, ketones, and esters. The aldehydes, as was shown in later pure compound studies (20) are easily and readily oxidized.

In all studies there was more extensive oxidation of both of the chloroform soluble fractions than of the alcohol fractions. These observations may be correlated with the fact that the chloroform fractions contained higher percentages of water soluble and neutral groups which consisted of materials shown to be easily oxidized. In addition to the aldehydes and esters of the neutral group, the keto acids of the water soluble group were shown to be readily oxidized in later pure compound studies. The alcohol fractions, in contrast, consist primarily of ether insoluble materials which are believed to be predominantly carboxylic acids, ketones, and alcohols of complicated structure (19). In a pure compound study (20) carboxylic acids, ketones, and aliphatic alcohols resisted oxidation under conditions similar to those used in this investigation.

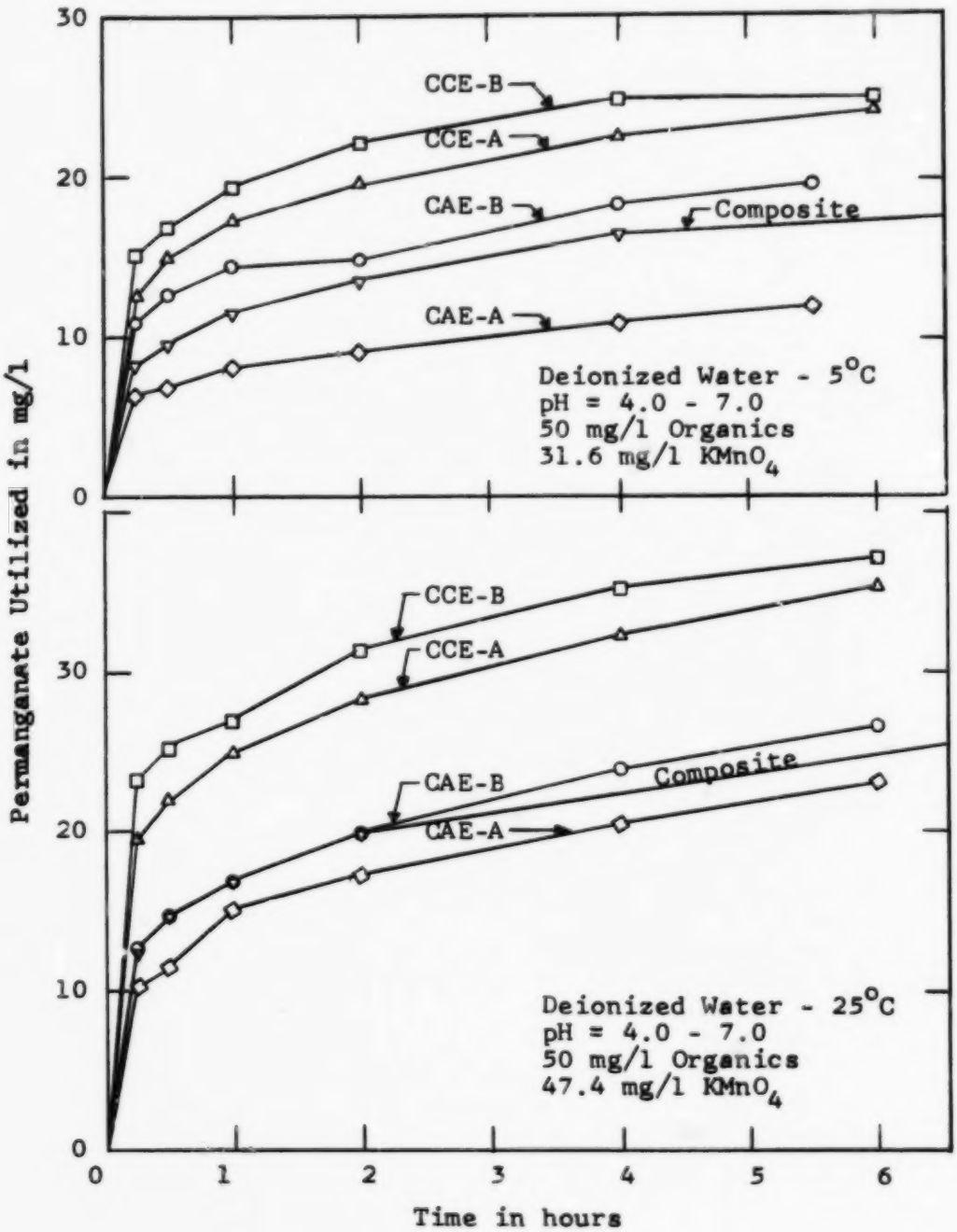

FIGURE 5

REACTIONS OF FIVE TYPES OF ORGANIC REFRACTORIES WITH POTASSIUM PERMANGANATE

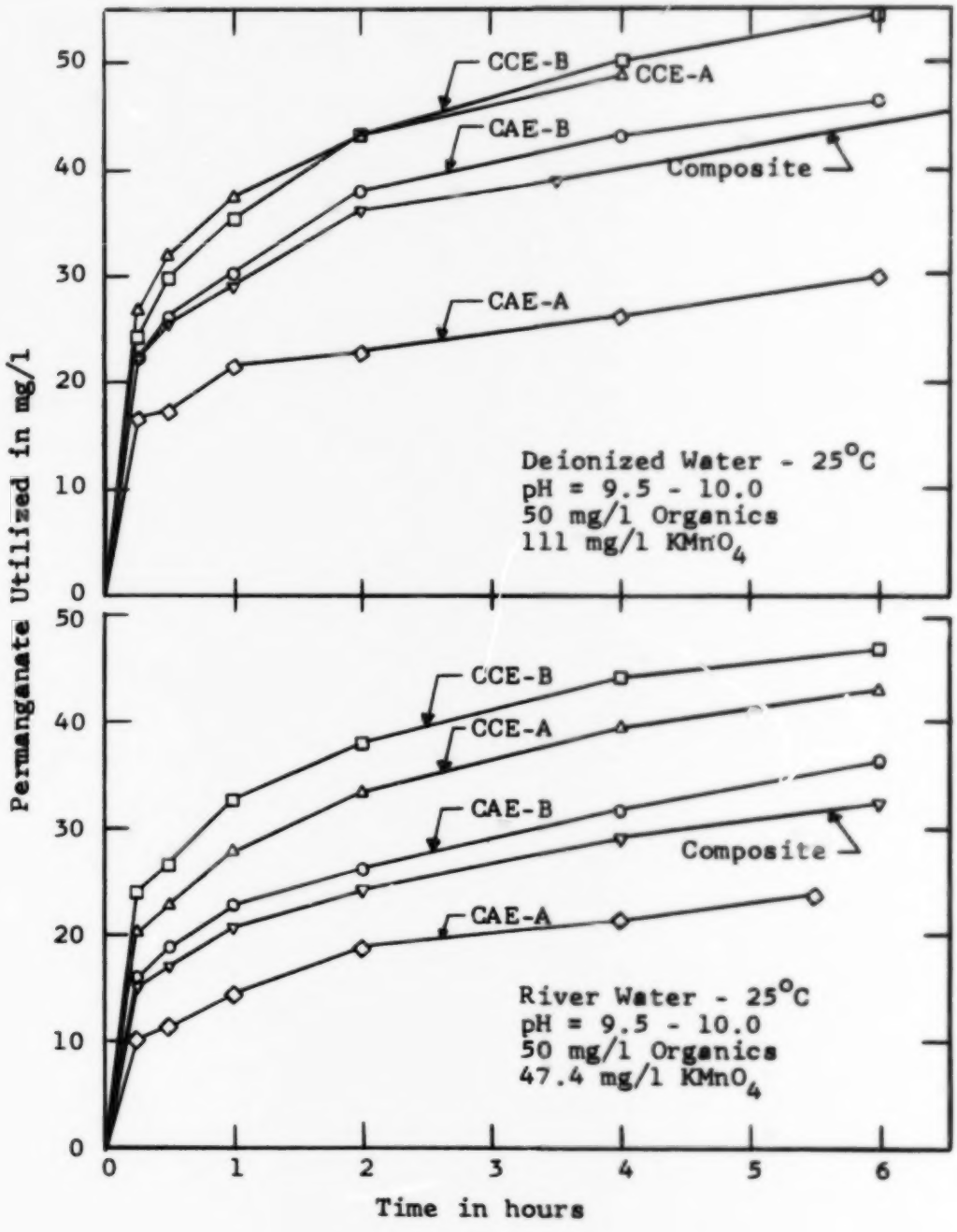

FIGURE 6

REACTIONS OF FIVE TYPES OF ORGANIC REFRACTORIES WITH POTASSIUM PERMANGANATE

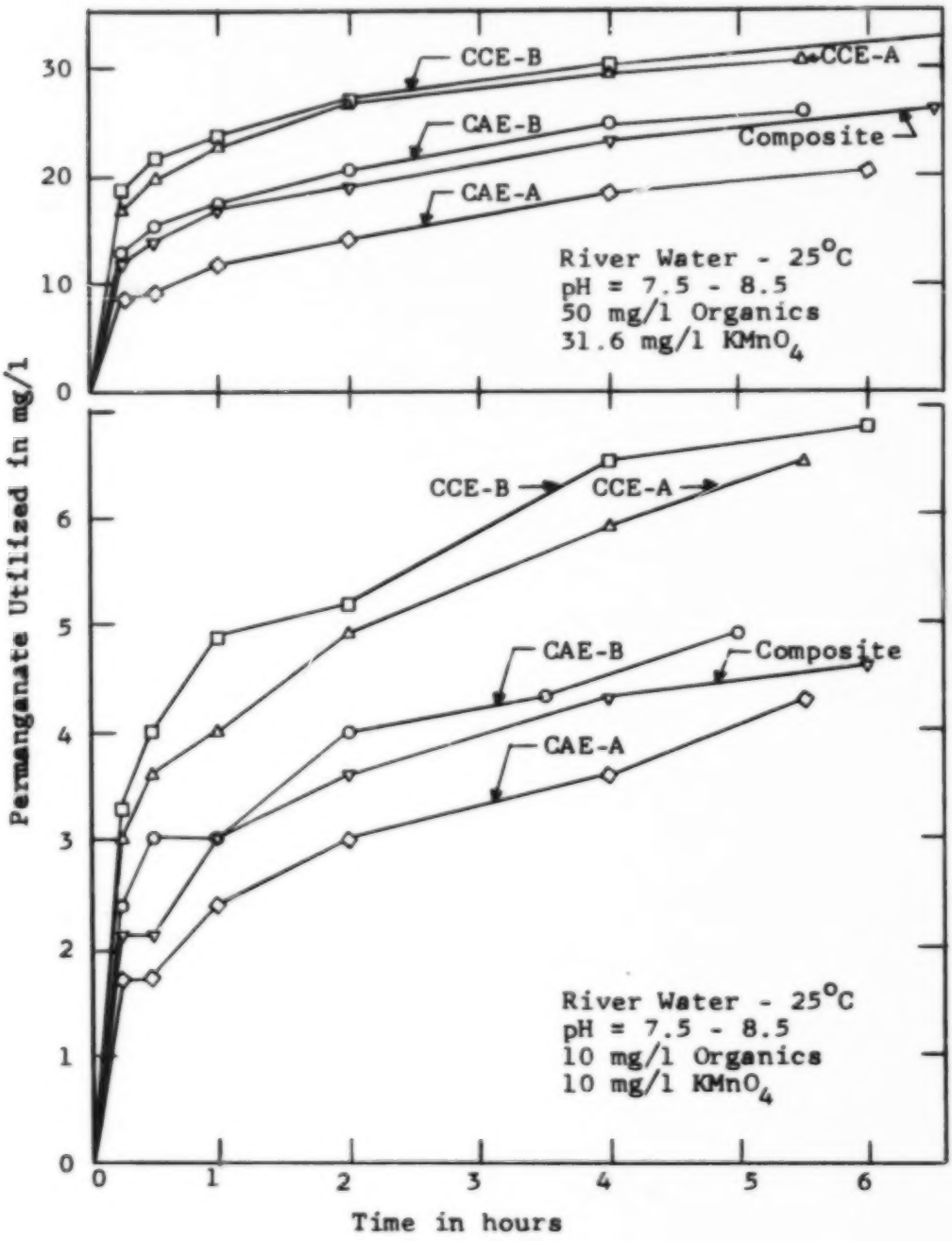

FIGURE 7

REACTIONS OF FIVE TYPES OF ORGANIC REFRACTORIES WITH POTASSIUM PERMANGANATE

The results also indicated that extracts recovered from the first carbon filter under basic conditions, the CCE-B and CAE-B were more amenable to oxidation than the extracts from the second carbon filter under acid conditions, the CCE-A and CAE-A.

It was noted that those organics which were most readily oxidized with potassium permanganate also exhibited the highest COD values. The permanganate utilized in a two-hour period was averaged for each organic fraction from the first six series of investigations at three levels of permanganate added. A ratio of these average values to the COD in mg/mg organics was then prepared. These calculations are shown in Table 5. The ratios for three of the fractions, CCE-B, CCE-A and CAE-B, were nearly the same, while that for the CAE-A fraction was substantially lower. The composite sample, which contained a large percentage of CAE-A, fell in between. Thus, there appears to be good correlation between COD and the amount of oxidation which occurs, particularly if the CAE-A fraction is considered separately.

Figures 8, 9 and 10 portray the effect of the concentration of potassium permanganate on the reaction. Curves are shown for 31.6, 47.4 and 111 mg/l of permanganate. Increasing the concentration of permanganate increased its utilization. The amount of oxidation, however, was not directly proportional to the concentration of permanganate added.

Plotting the average values for utilization of permanganate shown in Table 5 versus the permanganate added on a log-log

TABLE 5

RATIOS OF $KMnO_4$ UTILIZED TO COD

Average* Permanganate Utilization after Two Hours Reaction:

	Permanganate Added - mg/l		
	31.6	47.4	111
CCE-B	26.7	30.4	39.4
CCE-A	24.1	27.3	34.5
CAE-B	19.3	21.7	27.5
CAE-A	13.2	15.3	19.6
Composite	17.8	19.9	25.9

Chemical Oxygen Demand (COD):

CCE-B	1.87
CCE-A	1.66
CAE-B	1.36
CAE-A	1.29
Composite	1.38

Ratio of Permanganate Utilization after Two Hours to COD:

	Permanganate Added - mg/l		
	31.6	47.4	111
CCE-B	14.3	16.2	21.0
CCE-A	14.5	16.4	20.8
CAE-B	14.2	16.0	20.2
CAE-A	10.2	11.8	15.2
Composite	12.9	14.4	18.8

*Averages of the first six series of investigations

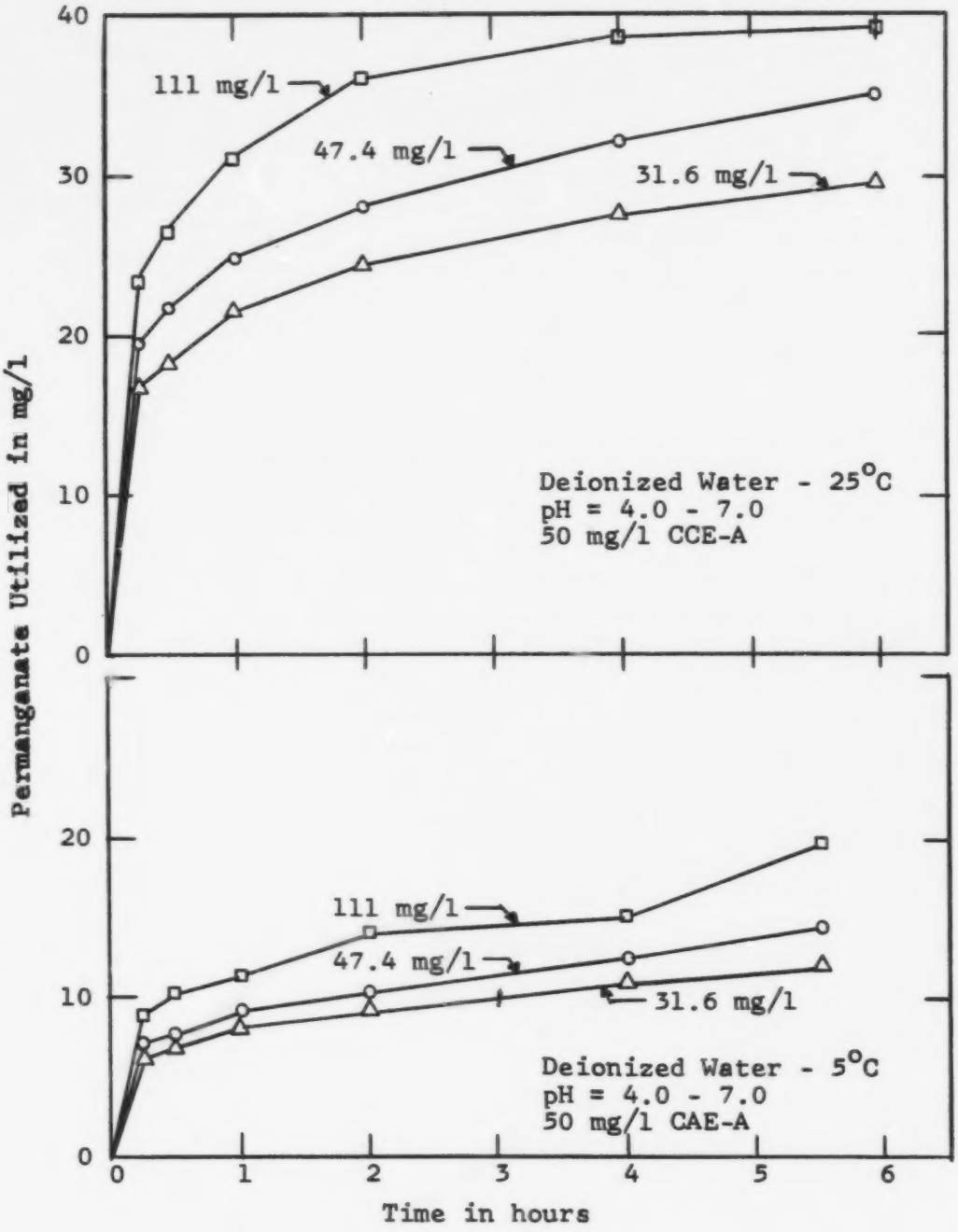

FIGURE 8

EFFECTS OF PERMANGANATE CONCENTRATION ON OXIDATION OF ORGANIC REFRACTORIES

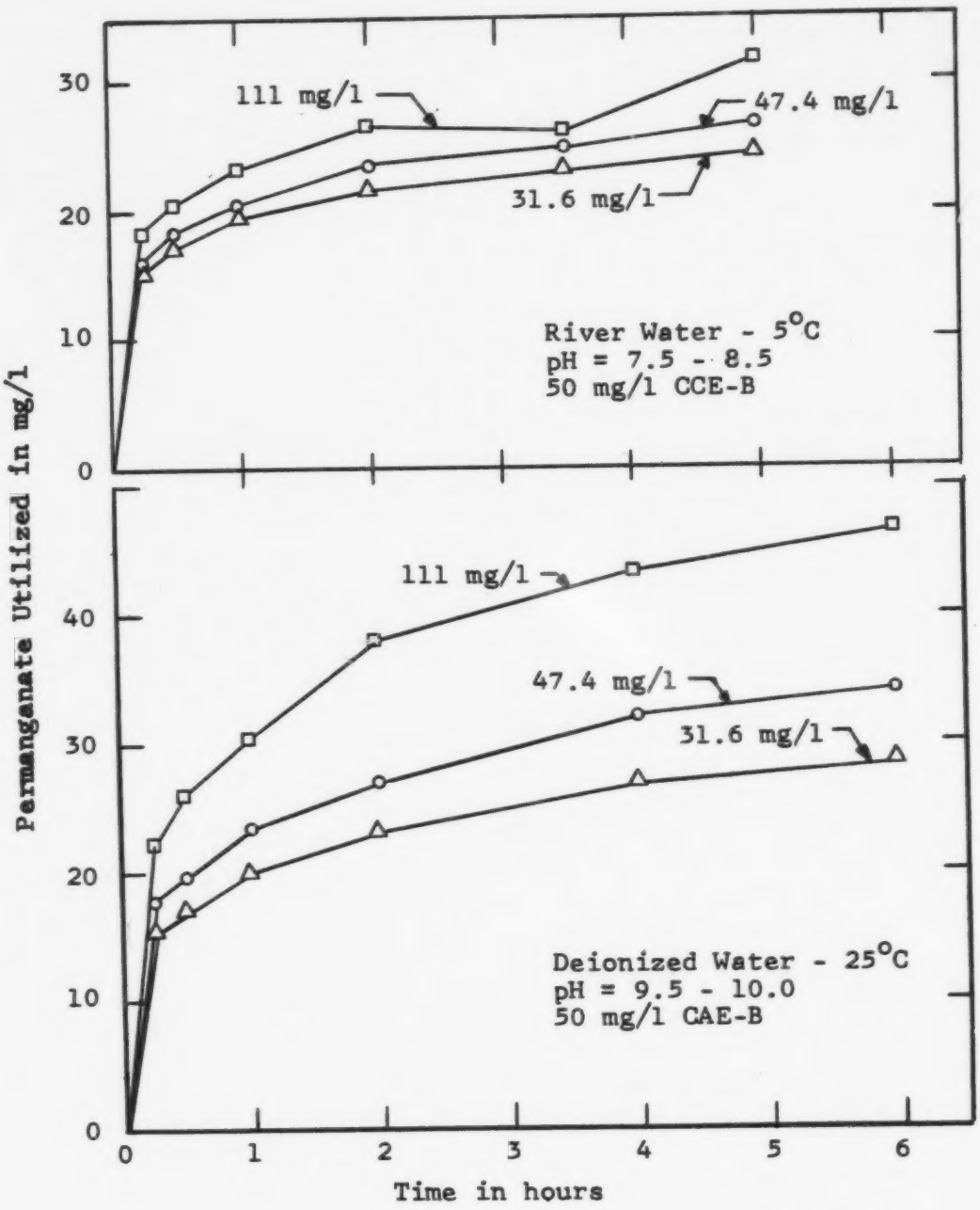

FIGURE 9

EFFECTS OF PERMANGANATE CONCENTRATION ON OXIDATION OF ORGANIC REFRACTORIES

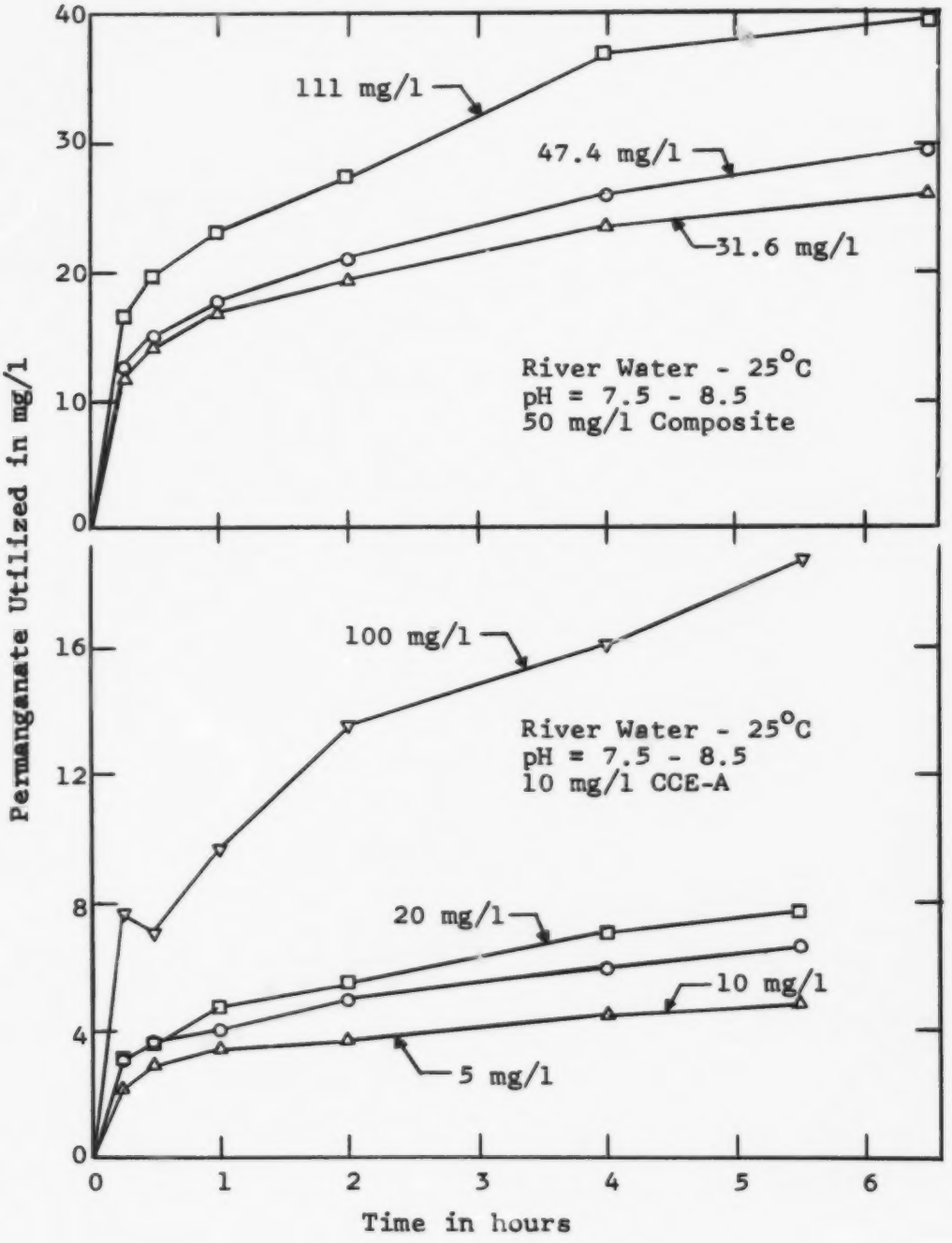

FIGURE 10

EFFECTS OF PERMANGANATE CONCENTRATION ON OXIDATION OF ORGANIC REFRACTORIES

plot showed the oxidation to be proportional to the amount of permanganate added to the 0.3 power (± 0.015) within the range of concentrations used in this investigation. These curves are shown in Figure 11. Equations for the curves would have the form: $y=kx^{0.3}$ where y=permanganate utilized in mg/l; x=permanganate added in mg/l; k=constant depending on the conditions of the reaction.

The effects of concentrations of organic refractories are shown in Figure 12. Curves representing two concentrations, 10 mg/l and 50 mg/l, are shown for each of the five types of organic refractories. Increasing the concentration of organic material increased the amount of permanganate entering into the reaction. Once again the increased utilization was not directly proportional to the increase in organic concentration. In this case not enough data were available to estimate the exponent of proportionality. However, by observation of the data it appears to be less than one.

That the reactions were temperature dependent is shown in Figure 13. The reaction curves at two temperatures, 5°C. and 25°C., are shown for six sets of conditions. That greater oxidation occurred at higher temperature was expected, since an increase in temperature generally increases the rate of a chemical reaction. It has been reported that many organic reactions are doubled for each 10° rise in temperature. In this investigation, however, as can be seen in Figure 13, the rate was not doubled for a 20° rise in temperature.

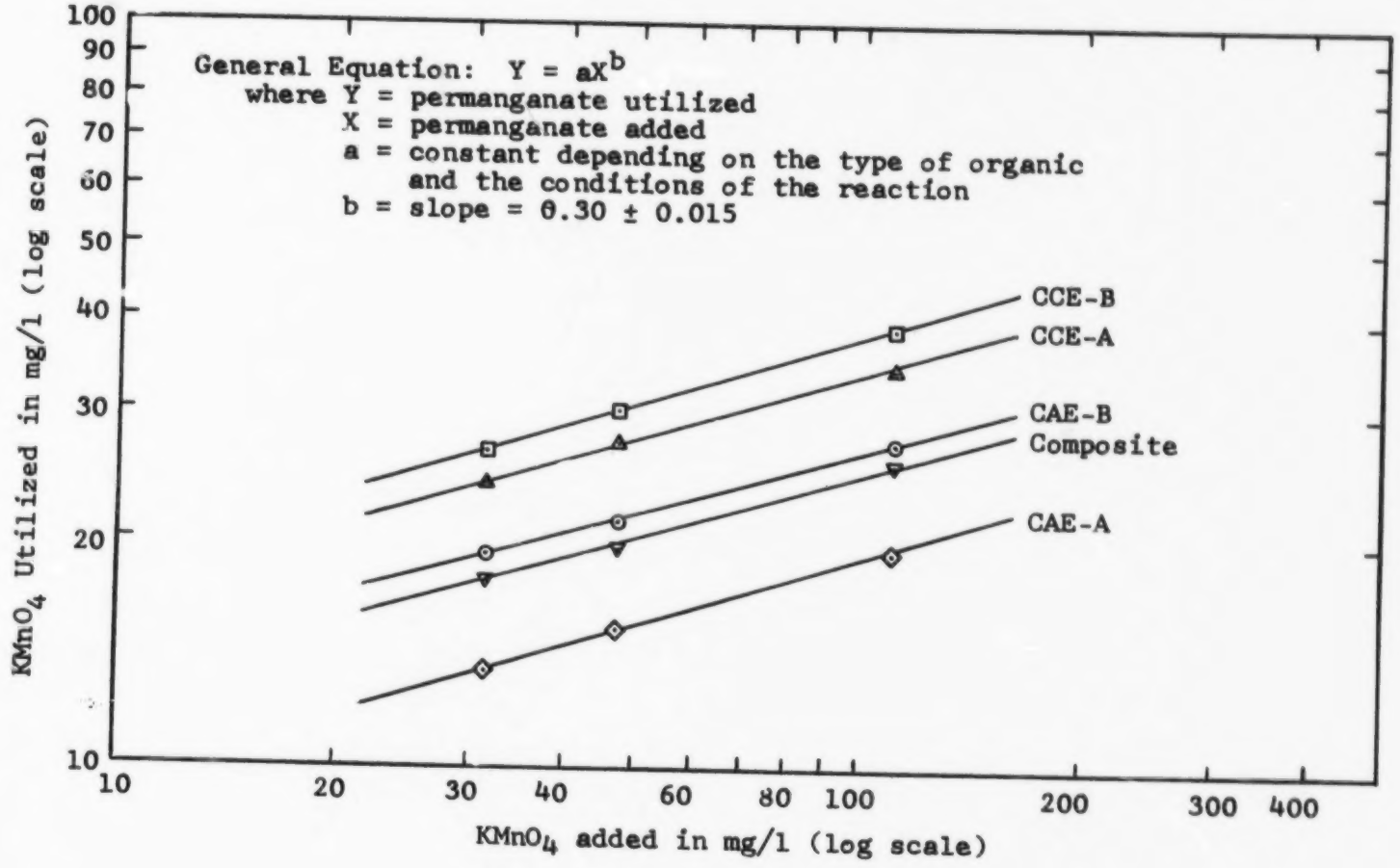

FIGURE 11

CORRELATION BETWEEN $KMnO_4$ UTILIZED AND $KMnO_4$ ADDED

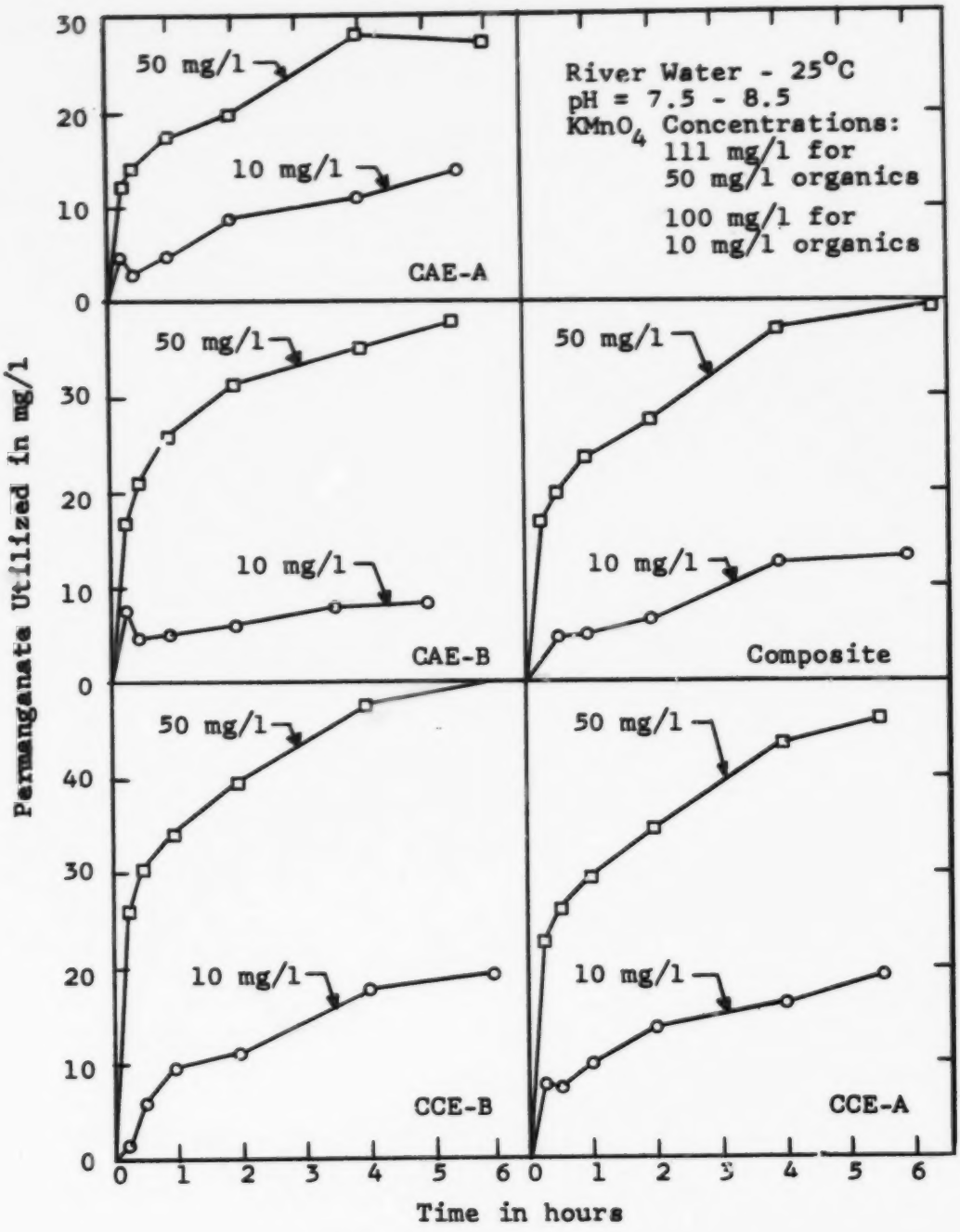

FIGURE 12

PERMANGANATE OXIDATION OF TWO CONCENTRATIONS OF ORGANIC REFRACTORIES

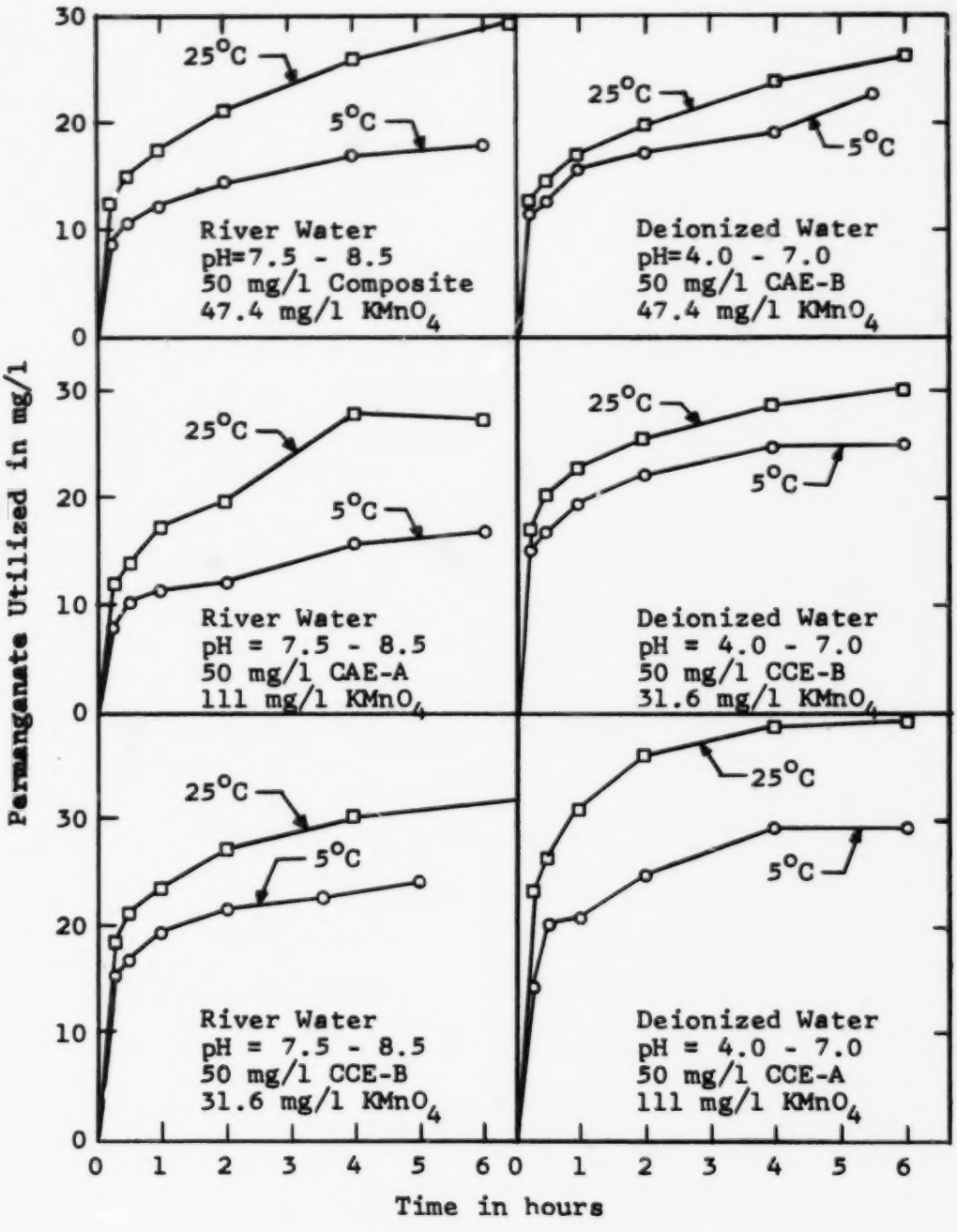

FIGURE 13

EFFECTS OF TEMPERATURE ON OXIDATION OF ORGANICS WITH POTASSIUM PERMANGANATE

The results illustrated in Figure 14 indicate the effect of pH on the oxidation of the organic refractories. Studies were made at pH values of 4.0-7.0, 7.5-8.5 and 9.5-10.0. Increasing the pH from near neutral values to a pH of 10 increased the amount of permanganate utilized. It thus appears that potassium permanganate is a more effective oxidizing agent under alkaline conditions than under neutral conditions.

Figure 15 shows that the reactions in a modified river water were essentially the same as those in distilled-deionized water. The inorganic constituents in the river water, therefore, exerted no significant effect on the reactions.

From the curves plotted in Figures 5 through 10 and 12 through 15, it is observed that the permanganate oxidation of organic refractories is not an instantaneous reaction, but rather one which depends on time of contact. Initially the rate of the reaction is high, and it decreases with time.

A possible explanation for the type of reaction is that the oxidation of organic matter probably occurs in a series of steps with the formation of intermediate products. An alcohol, for instance, is believed to be oxidized to an aldehyde and then to an acid. Each stage of the oxidation process may have a different reaction rate.

It is also probable that those compounds which resist reaction immediately upon contact with potassium permanganate will eventually, with time, react at least to a limited extent with the oxidizing agent. This was observed occasionally in those investigations when reactions were allowed to continue

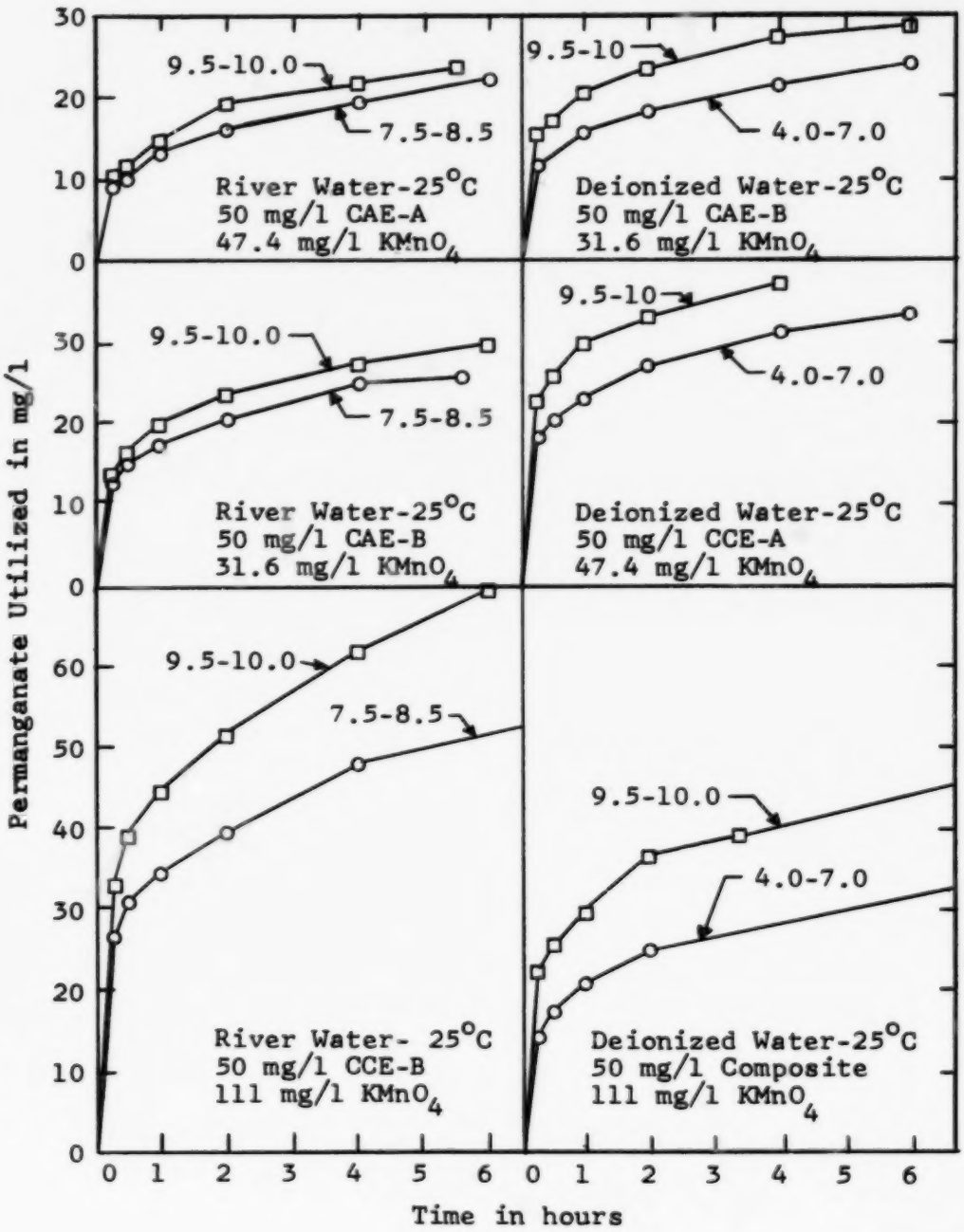

FIGURE 14

EFFECTS OF pH ON THE REACTION OF POTASSIUM PERMANGANATE WITH ORGANIC REFRACTORIES

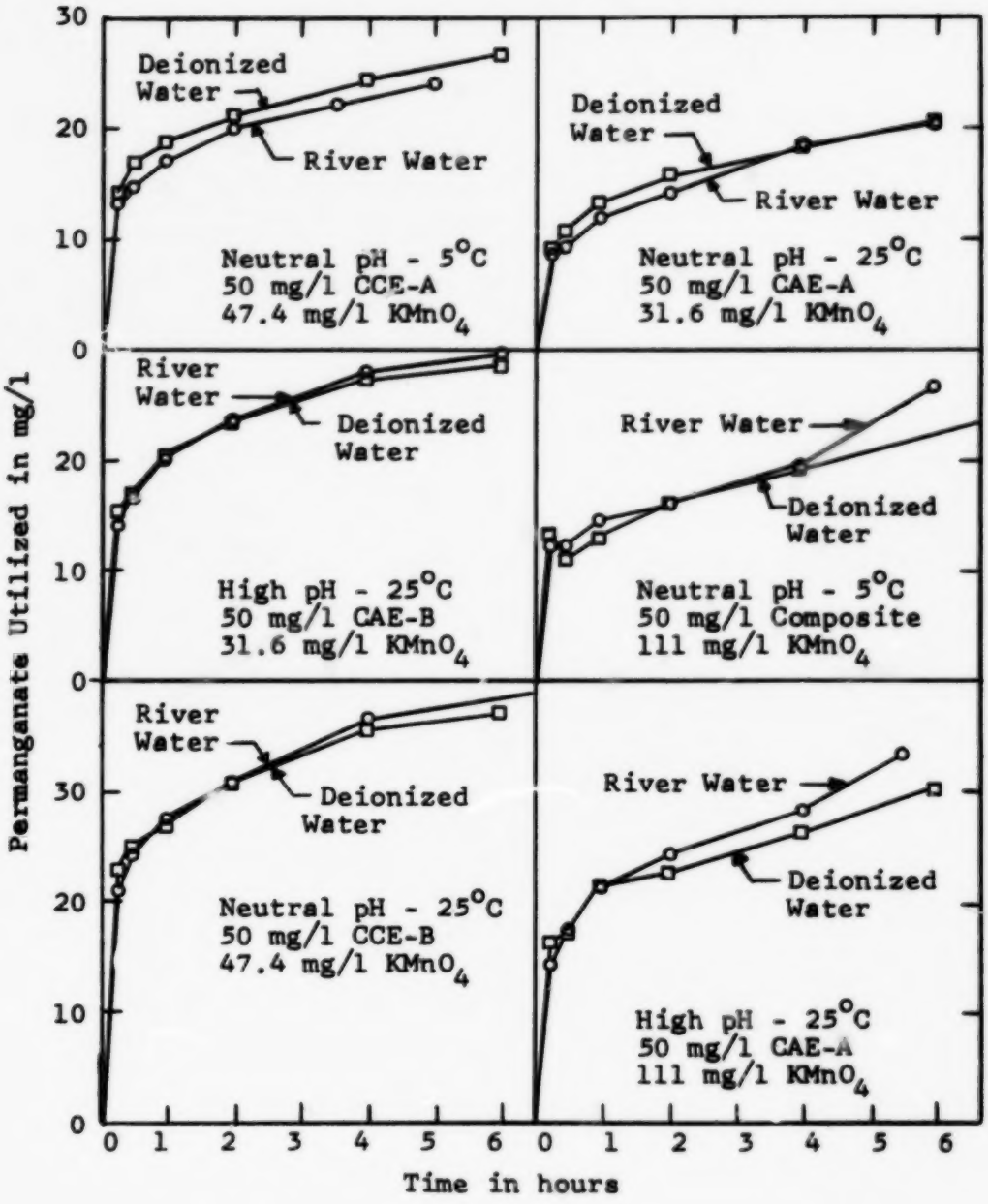

FIGURE 15

PERMANGANATE REACTION STUDIES
IN TWO TYPES OF WATER

for 24 hours or longer. Solutions which showed very little utilization after six hours often showed some utilization after several days as was noted by a change in color from the purple-pink of permanganate to the red, brown, or yellowish-brown of reaction products and reduced permanganate.

Threshold odor determinations were made on the samples after 2 hours of reaction time. A blank sample containing only the organic refractories and no potassium permanganate was used for comparison. The standard threshold odor test (16) was used for these determinations, with a panel of six experienced testers. Two pH conditions were used in the reactions: a near neutral pH and a pH near 10.

The results of the threshold odor determinations are presented in Figure 16. Oxidation with potassium permanganate reduced to some extent the odor potential of the organic refractory materials. Percent reductions ranged from 21 to 61 percent in the near neutral pH reactions, with an average of 46 percent. In reactions at pH near 10 the percent reduction range was 28 to 75 percent, with a 52 percent average.

Adding a phosphate buffer solution to raise the pH caused the threshold odor of the organic refractories to be reduced approximately 35 to 50 percent in the absence of permanganate. Permanganate addition then further reduced the threshold odor as described above at pH 10.

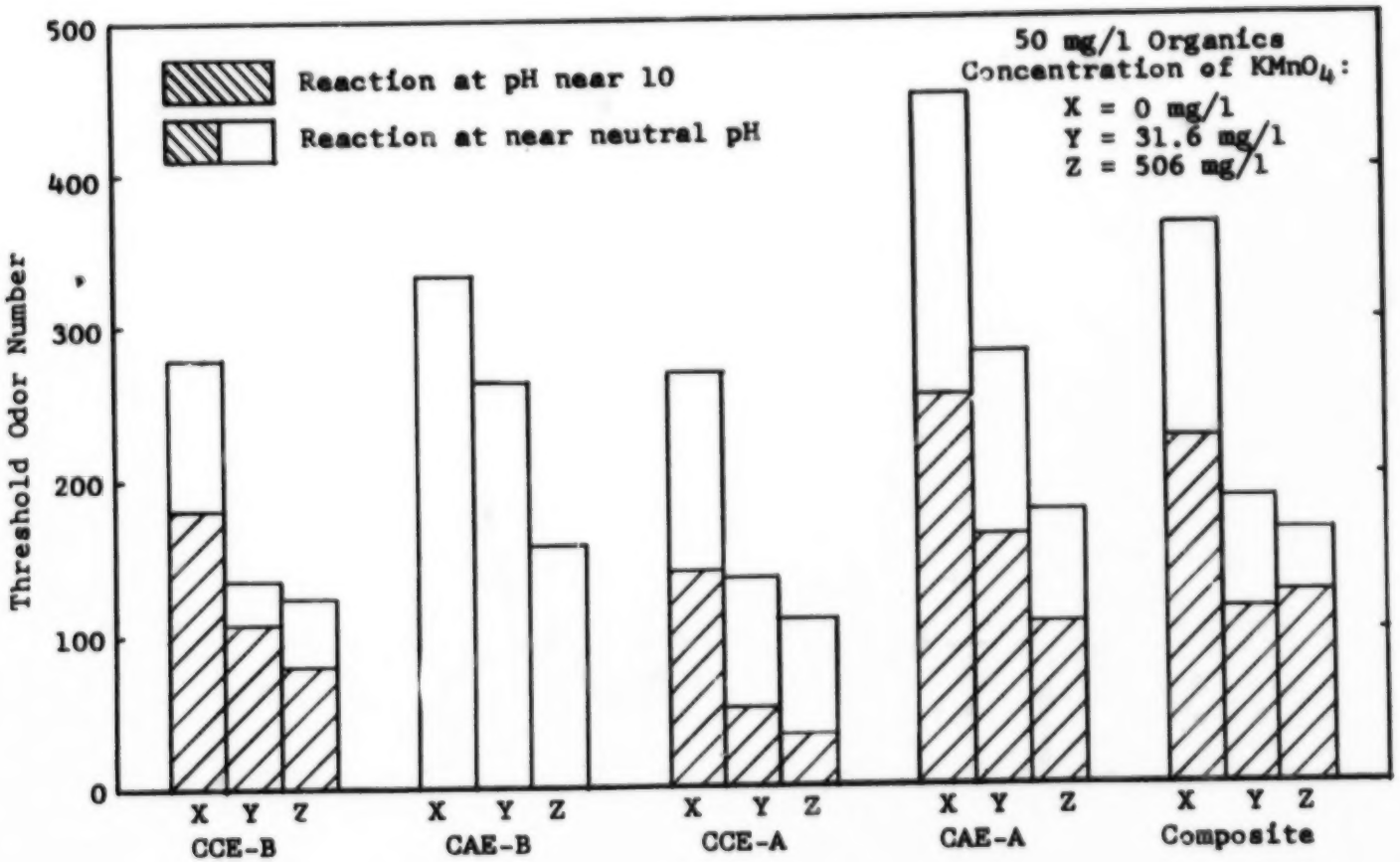

FIGURE 16

REDUCTION IN ODOR POTENTIAL OF NATURAL RIVER ORGANICS BY PERMANGANATE OXIDATION

SUMMARY

The results of this investigation showed limited oxidation of organic refractories with potassium permanganate. The rate of the reaction showed an approximate direct relationship to the concentration of permanganate remaining, thus most closely approaching a first-order reaction.

In this study reaction with potassium permanganate reduced the odor potential of organic refractories by approximately 50 percent. The reduction was similar for low and high concentrations of permanganate. This reduction in odor potential was not as great as most reductions reported in field studies where potassium permanganate was usually used in conjunction with other methods of taste and odor reduction.

No direct relationship was found between odor reduction and the permanganate oxidation of organic refractories. Incomplete oxidation of the organic materials could yield intermediate organic compounds which could exhibit greater or smaller odor potentials than the original reactants.

CONCLUSIONS

The following conclusions were reached based on the results of this investigation:

1. Lowering the pH of the effluent from the first carbon filter and passing the water through a second carbon filter in a two-filter series permitted recovery of at least twice as much organic refractories as with the first carbon filter alone.

2. The carbon alcohol extracts recovered exhibited higher odor potentials than the carbon chloroform extracts.
3. Tristimulus color determinations were made on organic refractory solutions and the four organic solutions analyzed in this investigation exhibited dominant wavelengths of 573 to 582 mu, with hues of greenish-yellow to yellowish-orange, respectively.
4. The CCE-B fraction was the most readily oxidized by potassium permanganate, followed in decreasing order by CCE-A, CAE-B, the composite, and CAE-A.
5. Organic refractories recovered from the first carbon filter (neutral or slightly alkaline water) were more amenable to oxidation with permanganate than those recovered from the second carbon filter (acidic conditions).
6. For three of the organic refractories, CCE-B, CCE-A, and CAE-B, a correlation was found between the chemical oxygen demand (COD) of the organic fraction and the extent of oxidation by permanganate. Those refractories with the highest COD exerted a greater utilization of permanganate.
7. The extent of oxidation of organic refractories, as measured by permanganate utilization after 2 hours, was found to be directly proportional to the 0.3 power of the amount of potassium permanganate added, within the range of concentrations used in this investigation.

8. Permanganate oxidation of organic refractories is a temperature-dependent reaction.
9. Potassium permanganate is a more effective oxidizing agent for organic refractories under alkaline conditions than under neutral conditions.
10. The inorganic constituents in natural river water had no apparent effect on the reaction of potassium permanganate with organic refractories.
11. The kinetics of the reaction of potassium permanganate with organic refractories approximated most closely those of a first-order reaction.
12. Potassium permanganate oxidation reduced the odor potentials of the 4 organic fractions by about 50 percent. The odor reduction did not vary significantly with increasing concentrations of permanganate.

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